Acta Futura 6 (2013) 37-42
DOI: 10.2420/AF06.2013.37

Acta Futura

Nacre: An Ancient Nanostructured Biomaterial

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Abstract. Nacre is a much appreciated natural material which forms in the interior of numerous mollusc shells. Its remarkable optical and mechanical properties are due to a highly nanostructured combination of inorganic and organic components, which has not been reproduced by any industrial process to date. In this paper we briefly review the current knowledge on the composition, structure, properties and mechanisms of formation of this iconic biomaterial.

1 Introduction

Nacre, most commonly known as mother-of-pearl, is a material exclusively secreted by molluscs which appeared on the Earth during the Paleozoic Era. First clear evidence of fossil nacre has been found in rocks formed in the late Ordovician, *i.e.* about 450 million years ago [6]. However, nacre might have an even earlier origin, since well-preserved fossils from the late Cambrian to the middle Ordovician are rare [18, 17]. The outstanding mechanical resistance of nacre suggests that this biomaterial evolved as a response to the increasing abilities and diversity of predators after the so-called Cambrian explosion, a unique event of animal diversification in the history of life. The development of claws, jaws and other novel tools of predation led to an arms race between predators and preys, which produced defensive adaptations such as toxicity, new escape methods (burrowing), camouflage, counter-offense, and armour. As a result of this ancient arms race, molluscs developed new crush-resistant shell microstructures, among which nacre is one of the most sophisticated and efficient. Recent paleontological studies indicate that molluscs "invented" nacre several times, *i.e.* nacre convergently evolved in at least four different classes of molluscs [18]. The significant differences in the microstructure and growth process of nacre between molluscan classes and the variation in both the genes and proteins associated with nacre in modern molluscs provide additional evidence that supports the independent origin of nacre within the Mollusca.

Numerous modern molluscs still produce different kinds of nacre. This natural product is a biocomposite, whose highly hierarchical structure and combination of inorganic and organic components, results in a material with unusual mechanical and optical properties [15, 13]. Until the industrial production of plastics, nacre was widely used in button-making, as construction material, and for decoration purposes (e.g. special

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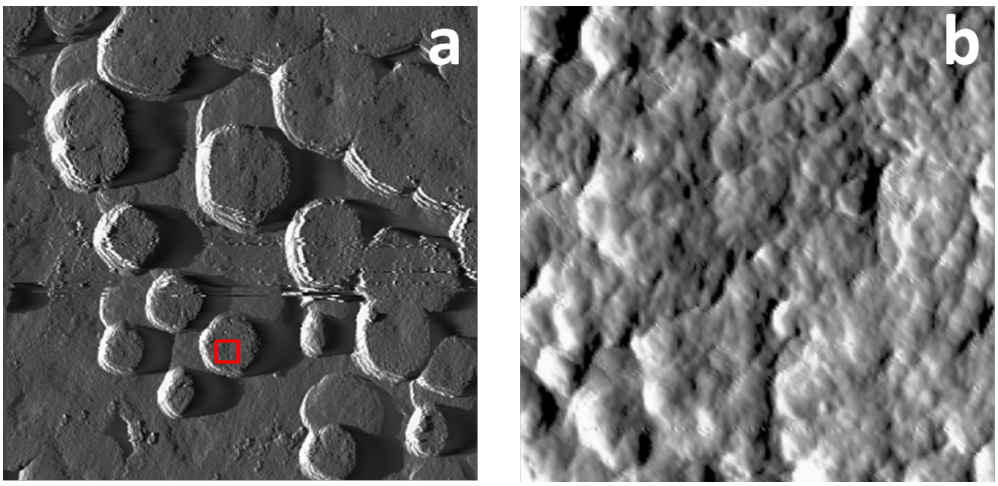

FIGURE 1. *AFM images taken in tapping mode while displaying the amplitude signal. (a) Aragonitic tablets that form the nacre of the mollusc Pteria hirundo. Note that the coalescence of tablets at the upper right results in a homogeneous mineralised layer. (Size of the image: 14.8×14.8 μm^2). (b) Detail of the surface of an aragonitic tablet (red square marked in (a)) showing the agglomerate of nanounits that form it. (Size of the image: 773×773 nm^2).*

tiles and glossy coatings of walls, doors and ceilings). When nacre is deposited in concentric layers around a foreign body in the interior of a mollusc, a pearl is produced. Pearls are appreciated objects in jewellery, whose commercial value depends on their size, perfection and roundness.

In the last few decades, nacre has attracted much attention in material science. Scientists and engineers have realized that nacre is a model material for a new generation of composite ceramics [1]. However, the development of nacre-bioinspired ceramics requires a profound knowledge of the relationships between composition, structure and properties of this ancient natural material.

2 The composition and structure of nacre

Nacre is composed of ≈ 95% of aragonite (orthorhombic $CaCO_3$) and ≈ 5% of a mixture of proteins and the polysaccharide chitin [10, 3]. In nacre, aragonite is in the form of polygonal tablets with a size ranging from 5 to 15 μm and a thickness of about 0.5 μm. Although the shape of the polygonal tablets varies from one species to another, in all the cases their surfaces are rough and formed by numerous mineral subunits of a few nanometres in diameter each (Fig. 1). In mollusc shells, aragonite tablets are arranged forming brickwall-like microstructures in which the organic matter (*i.e.* proteins and chitin) is the "mortar". The arrangement of aragonite tablets varies with the mollusc species and two main patterns can be recognised. While nacre secreted by gastropods is made of columns of tablets, in bivalves, layers of tablets are offset in successive step-like layers (Fig. 2).

3 Formation of nacre

The mechanism of nacre formation is not completely understood yet. Nacre is an extracellular material which forms between the external layer of the shell and the soft living body of the organism, *i.e.*, between a thick layer of calcite or aragonite crystals with a prismatic habit and the so-called mantle. There, one can find the extrapallial cavity, a micro-sized liquid-filled space where the self-assembly of aragonite tablets and organic matter occurs (Fig. 3). Recent authors have proposed a multi-step hierarchic mechanism of nacre formation [3, 4, 5]. Such a complex mechanism begins with the secretion of chitin molecules from the cells of the organism into the extrapallial cavity. These molecules polymerise forming rods of several microns in length which self-organise into a liquid crystal structure. Subsequently the chitin liquid crystal layer is coated by proteins resulting in the formation of an interlamellar membrane. This mem-

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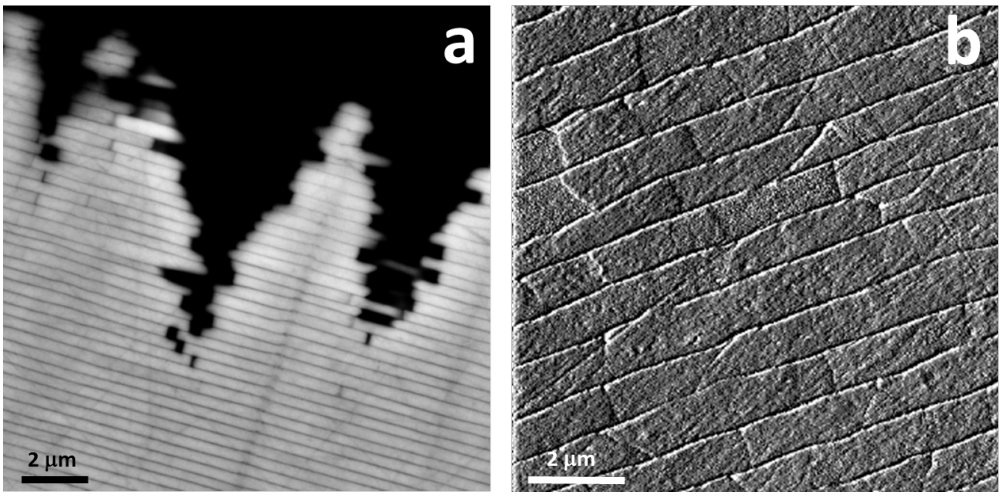

Figure 2. *Examples of the two nacre microstructures found in molluscs. (a) Columnar arrangement of aragonite tablets in the gasteropod Glibula umbilicalis (transmission electron microscopy image). (b) Sheet arrangement of aragonite tablets in the bivalve Neotrigonia margaritacea after the coalescence of tablets (amplitude atomic force microscopy image).*

brane is immersed in the extrapallial fluid which is supersaturated with respect to calcium carbonate. Then the growth of aragonite tablets occurs and the space between interlamellar membranes is progressively mineralised. However, the process leading to the growth and coalescence of aragonite tablets is not well known. Although numerous X-ray diffraction and transmission electron microscopy studies have confirmed the aragonitic nature of the tablets, the formation of amorphous calcium carbonate as a precursor phase of aragonite is still under investigation [19]. The high roughness of the aragonite tablets together with the observation of thin films coating them, suggest that the formation of the tablets takes place by accretion of aragonite nanounits covered by organic membranes. However, thin films might also appear as the result of the "exsolution" of organic molecules during the conversion of amorphous calcium carbonate into aragonite. The fact that the aragonite of nacre frequently incorporates fibrous proteins that previously were found in the interlamelar liquid seems to support both mechanism of tablet formation.

4 The properties of nacre

4.1 Mechanical properties

Nacre shows outstanding mechanical properties, which are superior to those of most common construction materials. As can be seen in Fig. 4, both types of nacre, columnar and sheet nacre, are much more resistant to tensile and compression stress than bricks, cement and concrete. In addition, nacre is significantly stiffer than these materials (*i.e.* it has a higher Young's modulus). Interestingly, nacre has a higher mechanical resistance than pure aragonite. It has been found that while the fracture toughness of nacre ranges from 3.3 to 9.0 $MPam^{1/2}$, the fracture toughness of inorganic aragonite crystals is approximately 1 $MPam^{1/2}$ [9, 14, 20, 8, 16]. The high toughness of nacre is comparable to advanced engineering materials and ceramic metal composites (cermets). This is remarkable considering that the 95% of nacre is made of the brittle mineral aragonite [1].

The mechanical properties of nacre also change with the degree of hydration. Thus, dry nacre behaves under tension elastically up to brittle failure, in a similar way as an aragonite single crystal does. In contrast, hydrated nacre, has an almost ductile response to tension. Such a response of nacre begins at tensile stresses of about 60-

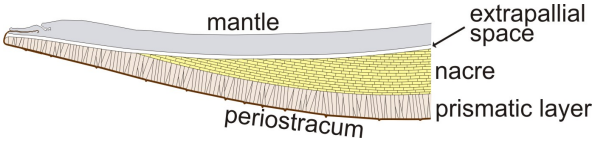

Figure 3. *Schematic drawing of the structure of a mollusc shell.*

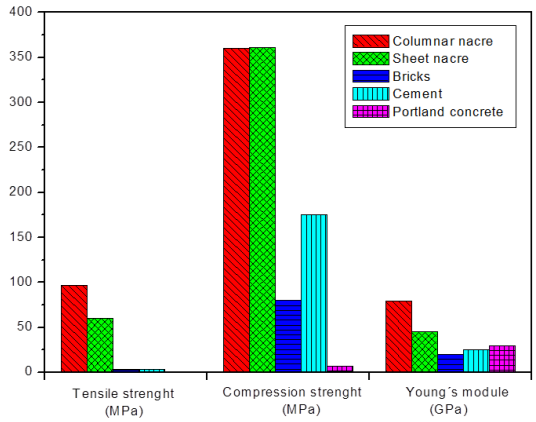

FIGURE 4. *Comparison between main mechanical properties of nacre and construction materials. Data for nacre are averaged from those in [7]. Data for construction materials are typical values found in the literature and internet sources.*

70 MPa, the deformation of the material at the brittle failure being of almost 1% [1]. This strain at the failure is low compared to many engineering materials but it is ten times higher than the strain at failure of aragonite. The ductile behaviour of wet nacre can be explained in terms of a collective sliding of aragonite tables at the microscale [16].

4.2 Optical properties

Undoubtedly, the most remarkable optical property of nacre is its iridescent shine. This shine is due to the fact that the thickness of the aragonite tablets is within the range of wavelengths of visible light (*i.e.* from 400 nm to 700 nm, approximately). As a consequence, light rays interfere constructively and destructively within the aragonite platelets depending on their incident angle. This angle-dependent interference generates different pale colours whose intensity varies with the position of the observer. The resulting effect is called structural coloration, since it is not related to any pigment but to a nanostructured reflective and refractive surface.

When nacre is arranged more or less concentrically, as is the case with pearls, propagation of light becomes more complex and diffraction, birefringence and scattering phenomena modify the iridescent shine [13]. These phenomena, combined with the presence of organic and inorganic impurities, play a major role in determining the variety and quality of the natural and cultivated pearls used in jewellery.

5 Synthetic analogues of nacre

The production of materials with similar properties to those of nacre is not an easy task. Even though complex fabrication methods have been used to obtain composites with the stiffness and toughness of nacre, none of them entirely reproduce all the mechanical properties of the natural material [1]. In all the cases, these synthetic composites are made of hard particles glued together with a much softer and ductile component. The key to achieving all the characteristic mechanical properties of nacre is the control of: (i) the size, thickness and orientation of the hard particles, (ii) the interfacial properties between hard and ductile components, and (iii) the formation of a self-assembled hierarchical microstructure. To this end, various fabrication techniques, which include layer-by-layer deposition, colloidal assembly and sintering, have been explored.

By using a layer-by-layer assembly technique, a "nacre-like" nanocomposite has been recently prepared from vinyl alcohol and Na^{+-} montmorillonite clay nanosheets [12]. The obtained material shows a laminar microstructure which is strong and flexible. Interestingly, the surfaces of this laminated nanocomposite are highly transparent, resembling those of nacre.

Colloidal assembly also resulted in an interesting way of fabricating materials inspired by nacre. Based on this technique, an alumina/chitosan polymer was synthesised to have a low ceramic content but with a structure and mechanical properties similar to nacre [2]. In this case, the aspect ratio of the alumina embedded in the chitosan matrix was essential to ensure an adequate tablet sliding when fracture occurs.

To date, the synthetic material closest to natural nacre is a composite made of alumina and polymethyl methacrylate (PMMA) [11]. To produce such a material a complex protocol is required. Firstly, microscopic particles with a specific size have to be produced from alumina powder and using ice platelets as a template. Only then a sintering process and the infiltration of PMMA are conducted. The result is a highly deformable composite with a remarkable toughness but still not as fracture resistant as that of nacre.

6 Conclusion

Although nacre has been intensively investigated during the last few decades, the origin of its valuable features, as well as the mechanisms of its formation, still remain incompletely understood. Further investigations

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are needed to elucidate the complex relationships between microstructure, composition and mechanical and optical properties of nacre. In addition, the sequence of processes which lead to a hierarchical self-assembly of organic and inorganic components still requires more material characterisations, experimental work and modelling. The acquisition of this knowledge is fundamental for mimicking all the properties of nacre. Only then, the microstructures and construction principles of nacre will be successfully transferred from nature to technology.

References

[1] F. Barthelat. Nacre from mollusk shells: a model for high-performance structural materials. *Bioinspiration & Biomimetics*, 5(3):035001, 2010.

[2] L. J. Bonderer, A. R. Studart, and L. J. Gauckler. Bioinspired design and assembly of platelet reinforced polymer films. *Science*, 319(5866):1069–1073, 2008.

[3] J. H. E. Cartwright and A. G. Checa. The dynamics of nacre self-assembly. *Journal of The Royal Society Interface*, 4(14):491–504, 2007.

[4] J. H. E. Cartwright, A. G. Checa, B. Escribano, and C. I. Sainz-Díaz. Spiral and target patterns in bivalve nacre manifest a natural excitable medium from layer growth of a biological liquid crystal. *Proceedings of the National Academy of Sciences*, 106(26):10499–10504, 2009.

[5] A. G. Checa, J. H. E. Cartwright, and M.-G. Willinger. The key role of the surface membrane in why gastropod nacre grows in towers. *Proceedings of the National Academy of Sciences*, 106(1):38–43, 2009.

[6] V. V. Druschits, L. Doguzhaeva, and V. G. Korinevskiy. Shell microstructure of the Ordovician monoplacophoran Romaniella Doguzhaeva, 1972. *Dokl. Akad. Nauk SSR*, 245:458–461, 1979.

[7] T. Furuhashi, C. Schwarzinger, I. Miksik, M. Smrz, and A. Beran. Molluscan shell evolution with review of shell calcification hypothesis. *Comparative Biochemistry and Physiology Part B: Biochemistry and Molecular Biology*, 154(3):351–371, 2009.

[8] K. E. Gunnison, M. Sarikaya, J. Liu, and I. A. Aksay. Structure-mechanical property relationships in a biological ceramic-polymer composite: Nacre. *MRS Online Proceedings Library*, 255, 0 1991.

[9] A. P. Jackson, J. F. V. Vincent, and R. M. Turner. The mechanical design of nacre. *Proceedings of the Royal Society of London. Series B. Biological Sciences*, 234(1277):415–440, 1988.

[10] Y. Levi-Kalisman, G. Falini, L. Addadi, and S. Weiner. Structure of the nacreous organic matrix of a bivalve mollusk shell examined in the hydrated state using Cryo-TEM. *Journal of Structural Biology*, 135(1):8–17, 2001.

[11] E. Munch, M. E. Launey, D. H. Alsem, E. Saiz, A. P. Tomsia, and R. O. Ritchie. Tough, bio-inspired hybrid materials. *Science*, 322(5907):1516–1520, 2008.

[12] P. Podsiadlo, A. K. Kaushik, B. S. Shim, A. Agarwal, Z. Tang, A. M. Waas, E. M. Arruda, and N. A. Kotov. Can nature's design be improved upon? high strength, transparent nacre-like nanocomposites with double network of sacrificial cross links. *The Journal of Physical Chemistry B*, 112(46):14359–14363, 2008.

[13] C. Raman and D. Krishnamurti. The structure and optical behaviour of iridescent shells. *Proceedings of the Indian Academy of Sciences - Section A*, 39(1):1–13, 1954.

[14] M. Sarikaya, K. E. Gunnison, M. Yasrebi, and I. A. Aksay. Mechanical property-microstructural relationships in abalone shell. *MRS Online Proceedings Library*, 174, 0 1989.

[15] J. Sun and B. Bhushan. Hierarchical structure and mechanical properties of nacre: a review. *RSC Adv.*, 2:7617–7632, 2012.

[16] J. Sun and J. Tong. Fracture toughness properties of three different biomaterials measured by nanoindentation. *Journal of Bionic Engineering*, 4(1):11–17, 2007.

[17] M. J. Vendrasco, A. Checa, W. P. Heimbrock, and S. D. Baumann. Nacre in molluscs from the ordovician of the midwestern united states. *Geosciences*, 3(1):1–29, 2013.

[18] M. J. Vendrasco, A. G. Checa, and A. V. Kouchinsky. Shell microstructure of the early bivalve pojetaia and the independent origin of nacre within the mollusca. *Palaeontology*, 54(4):825–850, 2011.

[19] S. Weiner, Y. Levi-Kalisman, S. Raz, and L. Addadi. Biologically formed amorphous calcium carbonate. *Connective Tissue Research*, 44(1):214–218, 2003.

[20] M. Yasrebi, G. H. Kim, K. E. Gunnison, D. L. Milius, M. Sarikaya, and I. A. Aksay. Biomimetic processing of ceramics and ceramic-metal composites. *MRS Online Proceedings Library*, 180, 0 1990.

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